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Am(III)/Nd(III) Interactions with Borate: Experimental Investigations of $Nd(OH)_3$(micro cr) Solubility in Mixtures of NaCl and $MgCl_2$ in Equilibrium with Borax (Invited)

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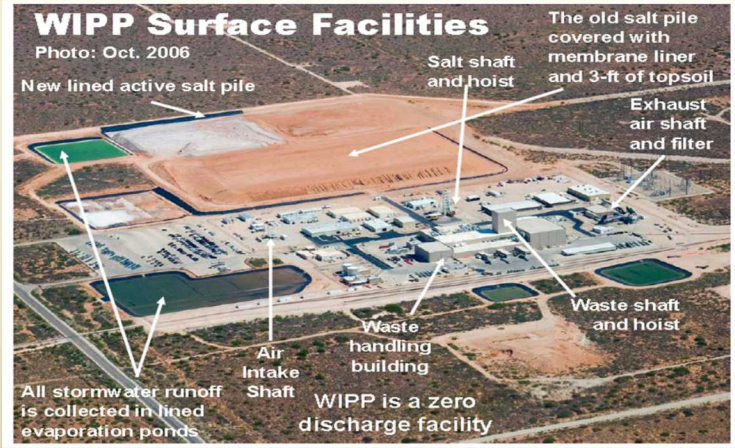
OUTLINE OF PRESENTATION

- Introduction
- Objective of This Work
- Experimental Method
- WIPP Borate Model
- Experimental Results
- Summary

INTRODUCTION

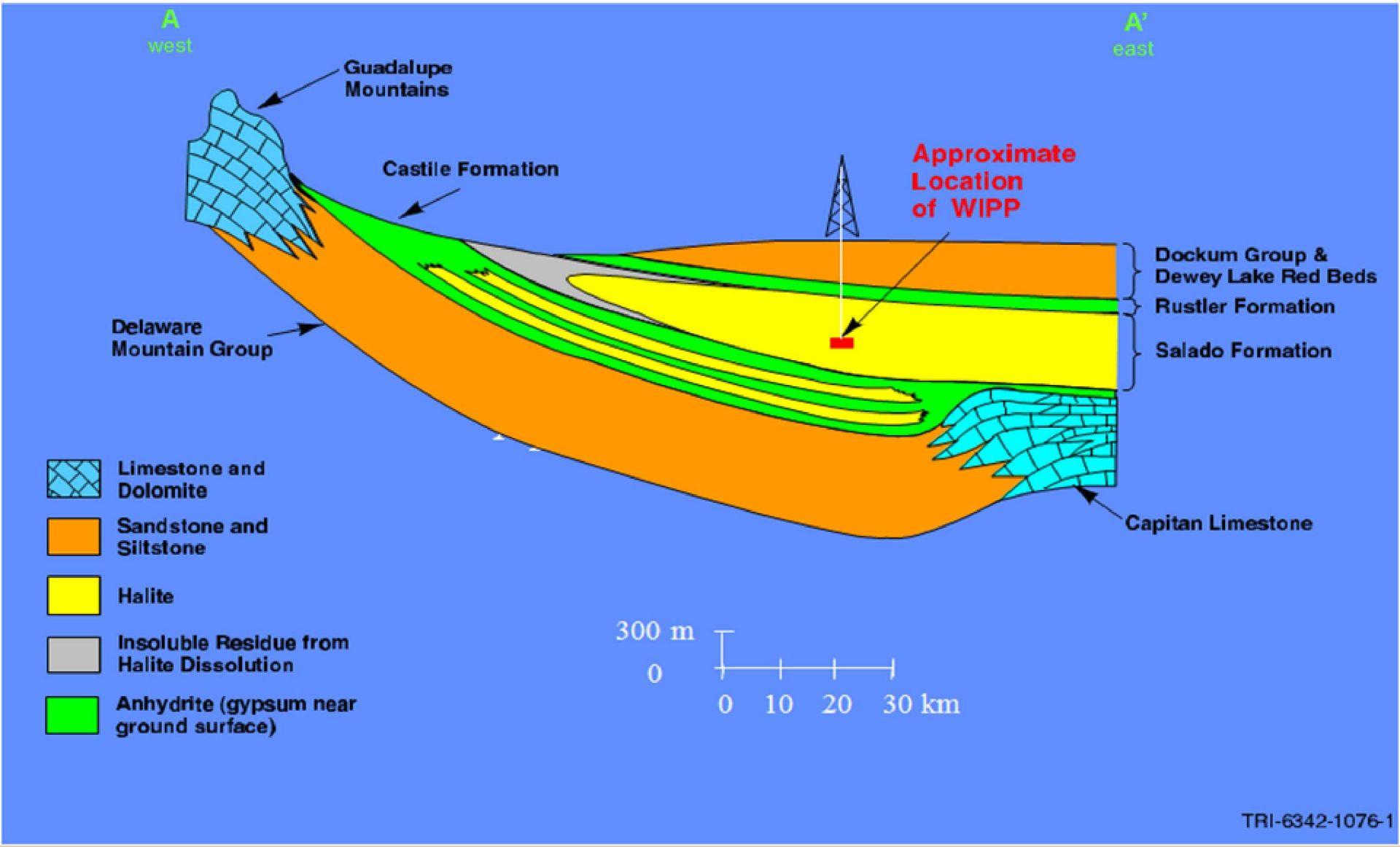
- The accurate knowledge of actinide solubilities that could be dissolved in natural brines is important to safe disposal of nuclear waste.
- Recent experimental work indicates that borate could form a relatively strong complex with Nd(III) ($NdHB_4O_7^{2+}$, $\log \beta_1 = 4.99 \pm 0.30$) at 25°C [1]. Nd(III) is used as an analog to Am(III) on the WIPP.
- Therefore, the assessment of contributions of borate complexation to solubility of Am(III) is needed.
- Borate is a species with significantly high concentrations in natural brines:
  - The borate concentrations in the Waste Isolation Pilot Plant (WIPP) brines
    - Generic Weep Brine (GWB): 0.180 mol•kg^{-1} and
    - U.S. Energy Research and Development Administration Well 6 (ERDA-6): 0.0692 mol•kg^{-1} [2]



[1] Borkowski, M., Richmann, M., Reed, D.T., and Xiong, Y.-L., 2010. Complexation of Nd(III) with tetraborate ion and its effect on actinide(III) solubility in WIPP brine. Radiochimica Acta 98, 577-582.

[2] Xiong, Y.-L., Lord, A.C., 2008. Experimental investigations of the reaction path in the $MgO–CO_2–H_2O$ system in solutions with various ionic strengths, and their applications to nuclear waste isolation, Applied Geochemistry, Vol.23, p. 1634.

WASTE ISOLATION PILOT PLANT (WIPP)



OBJECTIVE OF THIS STUDY

- To measure solubility of $Nd(OH)_3$(micro cr) in mixtures of NaCl + $MgCl_2$ saturated with borax ($Na_2B_4O_7 \bullet 10H_2O$) at 25°C in long-term experiments
- The reason for performing experiments at high borate concentrations saturated with borax:
  - It has been observed that tincalconite ($Na_2B_4O_7 \bullet 5H_2O$) can form when borosilicate glasses as waste form for high level nuclear waste (HLW) are corroded under the repository conditions [3].
  - Borax has the same solubility as tincalconite in terms of borate.
  - A previous study [4] was conducted at much lower borate concentrations; therefore the effect of borate on solubility of $Nd(OH)_3$(micro cr) has not been fully assessed.

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[3] Zhang, Z., Gan, X., Wang, L. and Xing, H., 2012. Alteration Development of the Simulated HLW Glass at High Temperature in Beishan Underground Water. *International Journal of Corrosion*, *2012*.

[4] K. Hinz, M. Altmaier, X. Gaona, T. Rabung, D. Schild, M. Richmann, D.T. Reed, E.V. Alekseev, and H. Geckeis, H., New journal of chemistry 39, 849 (2015).

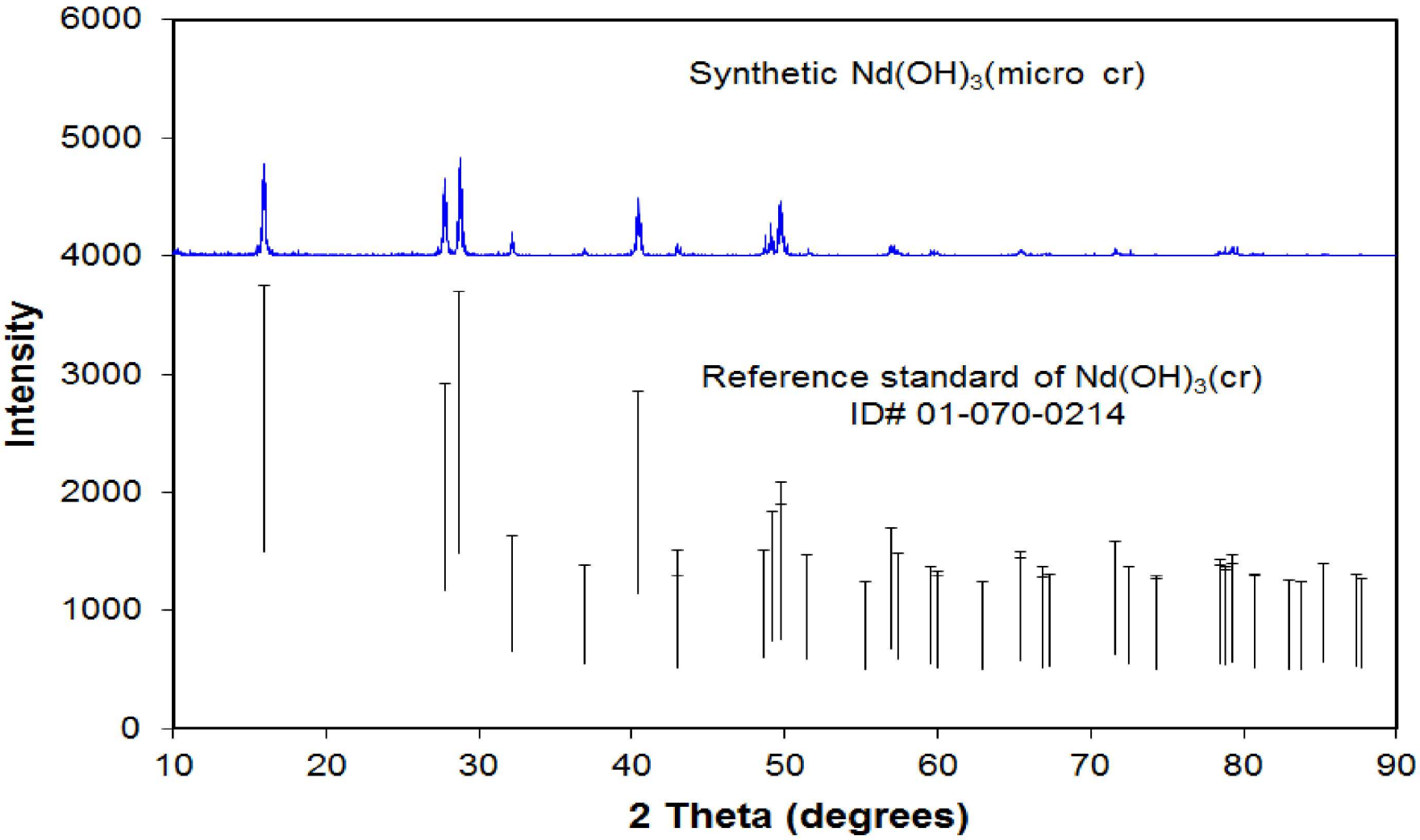
EXPERIMENTAL METHOD

- Experimental Apparatus: All experiments are conducted in a glovebox under N_2 + H_2 atmosphere in which oxygen and CO_2 are excluded.
- Experimental conditions: T = 25°C
- Starting material: Synthetic $Nd(OH)_3$(micro cr)
- Hydrogen ion concentrations (pH_m, molal scale) of the experimental systems are controlled/buffered by solubility of $Nd(OH)_3$(micro cr).
- pH_m are determined by applying correction factors to pH readings obtained using a pH meter.
- Nd(III) concentrations are analyzed using ICP-MS.
- Na and boron concentrations are analyzed using ICP-AES.
- Chloride concentrations are analyzed using IC.
- Approaching equilibrium from undersaturation
- Supporting solutions:
  - Mixtures of NaCl and $MgCl_2$ with ionic strengths up to 6.75 $mol \bullet kg^{-1}$

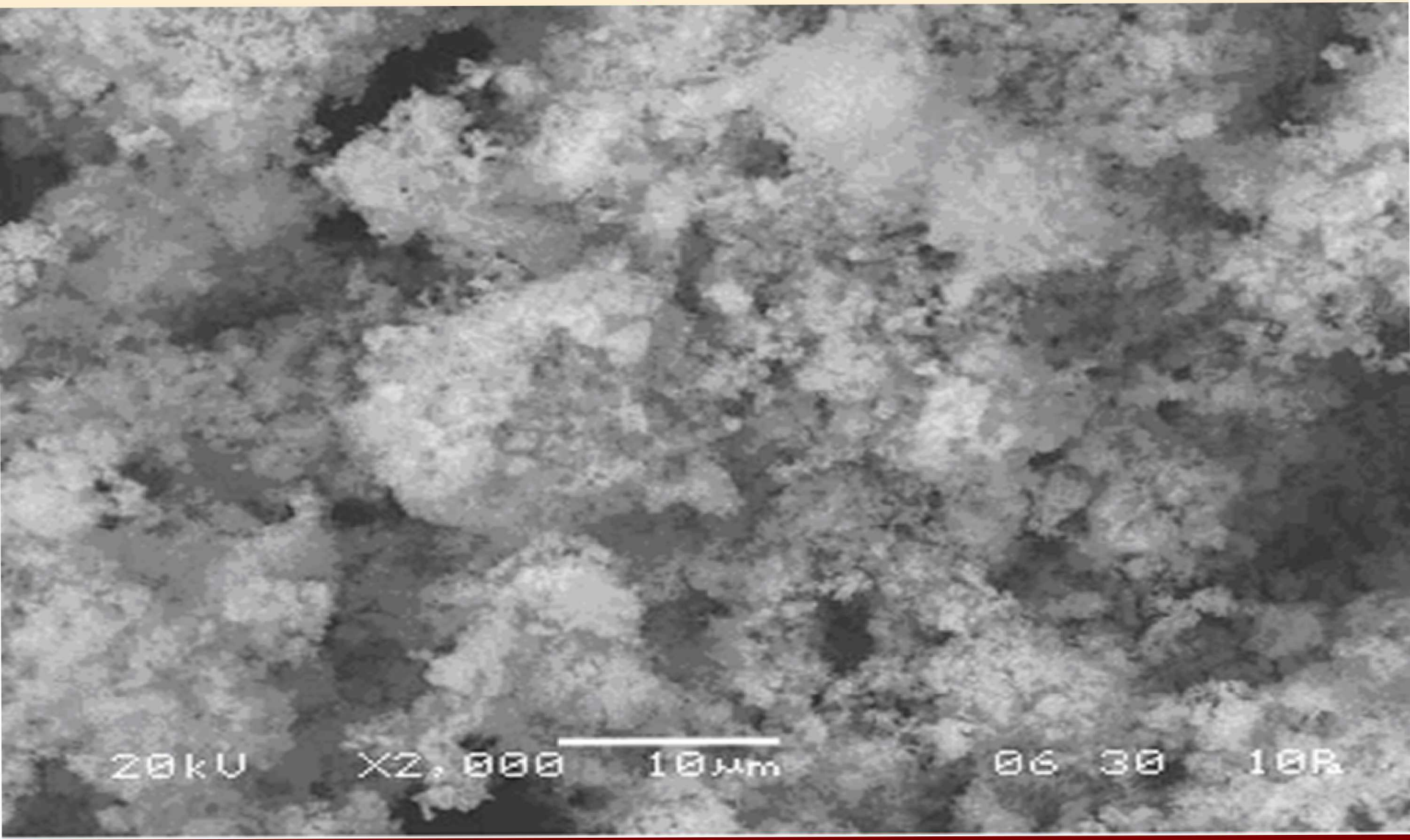
EXPERIMENTAL METHOD: Synthesis of $Nd(OH)_3$(micro cr)

- Having well-defined starting material with high purity is of fundamental importance to the success of solubility experiments.
- High purity Nd_2O_3 is first loaded with deaerated DI water into Paar® reaction vessels, and then the reaction vessels are sealed, in a glovebox under a positive pressure of the inert gas
- The reaction vessels are taken out from the glovebox, and are placed into a muffle furnace.
- $Nd(OH)_3$(micro cr) is synthesized by reacting high purity Nd_2O_3 with deaerated DI water at 200°C in Parr® reaction vessels for a period of two weeks.
- The reaction vessels are put back into the glovebox, and opened. The synthesized $Nd(OH)_3$(micro cr) is dried in the glovebox.

XRD Pattern of Starting Material: $Nd(OH)_3$(micro cr)



SEM Image of Starting Material: $Nd(OH)_3$(micro cr)



The WIPP Borate Model

Table 1. The WIPP borate model for the Na–$B(OH)_3$–Cl system (from DATA0.FM2) used for evaluation of formation constant for $AmHB_4O_7^{2+}$

Pitzer Binary Interaction Cofficients					
Species, *i*	Species, *j*	$\beta^{(0)}$	$\beta^{(1)}$	C^{ϕ}	Reference
Na^+	$B(OH)_4^-$	–0.0427	0.089	0.0114	[5]
Na^+	$B_3O_3(OH)_4^-$	–0.056	–0.910		[5]
Na^+	$B_4O_5(OH)_4^{2-}$	–0.11	–0.40		[5]
Pitzer Mixing Parameters and Interaction Parameters Involving Neutral Species					Reference
Species, *i*	Species, *j*	Species, *k*	θ_{ij} or λ_{ij}	Ψ_{ijk} or ζ_{ijk}	[5]
$B(OH)_4^-$	Cl^-	Na^+	–0.065	–0.0073	[5]
$B_3O_3(OH)_4^-$	Cl^-	Na^+	0.12	–0.024	[5]
$B_4O_5(OH)_4^{-2}$	Cl^-	Na^+	0.074	0.026	[5]
$B(OH)_3$(aq)	Cl^-		0.091		[5]
$B(OH)_3$(aq)	$B_3O_3(OH)_4^-$		–0.20		[5]
$B(OH)_3$(aq)	Na^+		–0.097		[5]
$NaB(OH)_4$(aq)	Na^+		0.093		[6]
Equilibrium Constant for Complex Formation					
Reaction			log K		Reference
$Na^+ + B(OH)_4^- = NaB(OH)_4$(aq)			0.25		[6]

[5] Felmy, A.R., and Weare, J.H. (1986) The prediction of borate mineral equilibria in natural waters: Applications to Searles Lake, California. Geochimica et Cosmochimica Acta, 50, no. 12, 2771–2783.

[6] Xiong, Y.-L., Kirkes, L., and Westfall, T., 2013. Experimental Determination of Solubilities of Sodium Tetraborate (Borax) in NaCl Solutions, and A Thermodynamic Model for the Na–$B(OH)_3$–Cl–SO_4 System to High Ionic Strengths at 25 °C. American Mineralogist 98, 2030–2036.

Equilibrium Constants Consistent with the WIPP Borate Model (from [7])

Table 2. Equilibrium constant for $AmHB_4O_7^{2+}$ at infinite dilution at 25 °C (298.15 K), and its associated Pitzer interaction parameters

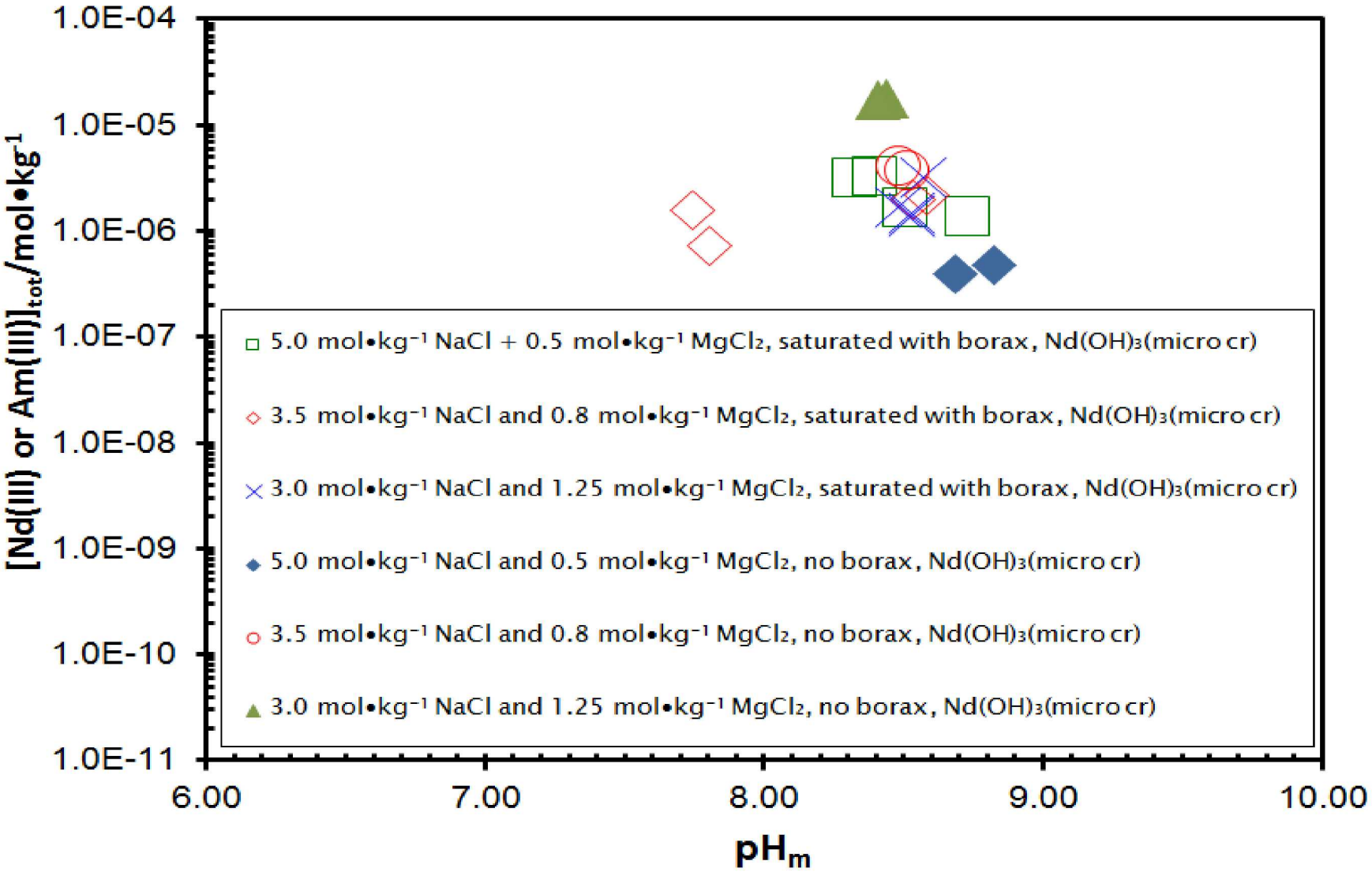
Reaction			log K at 25 °C	
$4B(OH)_4^- + 3H^+ + Am^{3+} \rightleftharpoons AmHB_4O_7^{2+} + 9H_2O(l)$			37.3416	
Pitzer Binary Interaction Cofficients				
Species *i*	Species *j*	$\beta^{(0)}$	$\beta^{(1)}$	C^{ϕ}
$AmHB_4O_7^{2+}$	Cl^-	0.9163	1.74	0

Table 3. Equilibrium constant for $AmB_9O_{13}(OH)_4(cr)$ at infinite dilution at 25 °C (298.15 K)

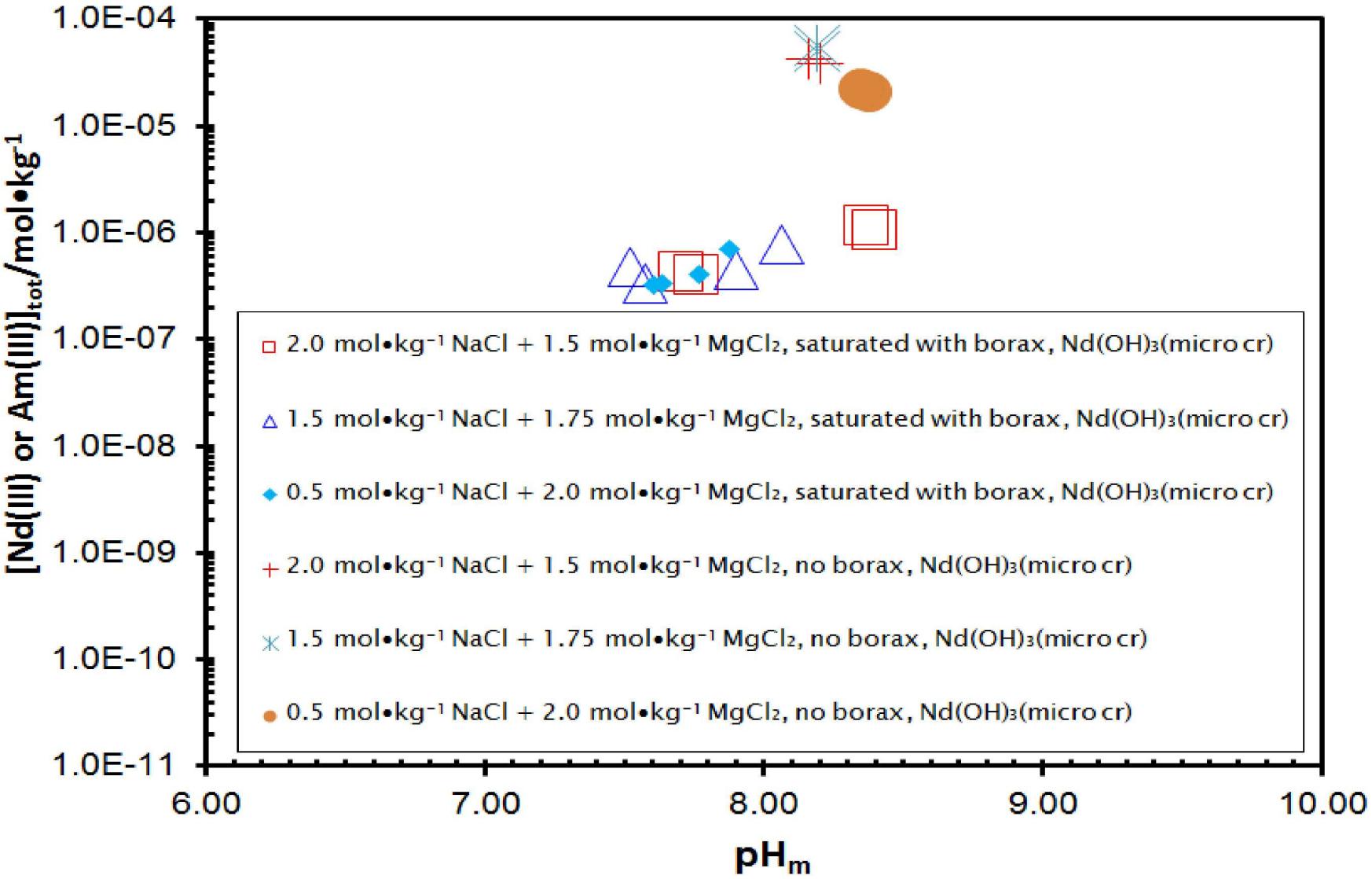
Reaction	log K at 25 °C
$AmB_9O_{13}(OH)_4(cr) + 19H_2O(l) \rightleftharpoons Am^{3+} + 9B(OH)_4^- + 6H^+$	–79.00±0.30

[7] Xiong, Y., 2017. Solution Chemistry for Actinide Borate Species to High Ionic Strengths: Equilibrium Constants for $AmHB_4O_7^{2+}$ And $AmB_9O_{13}(OH)_4(cr)$ and Their Importance to Nuclear Waste Management. *MRS Advances*, *2*(13), pp.741-746.

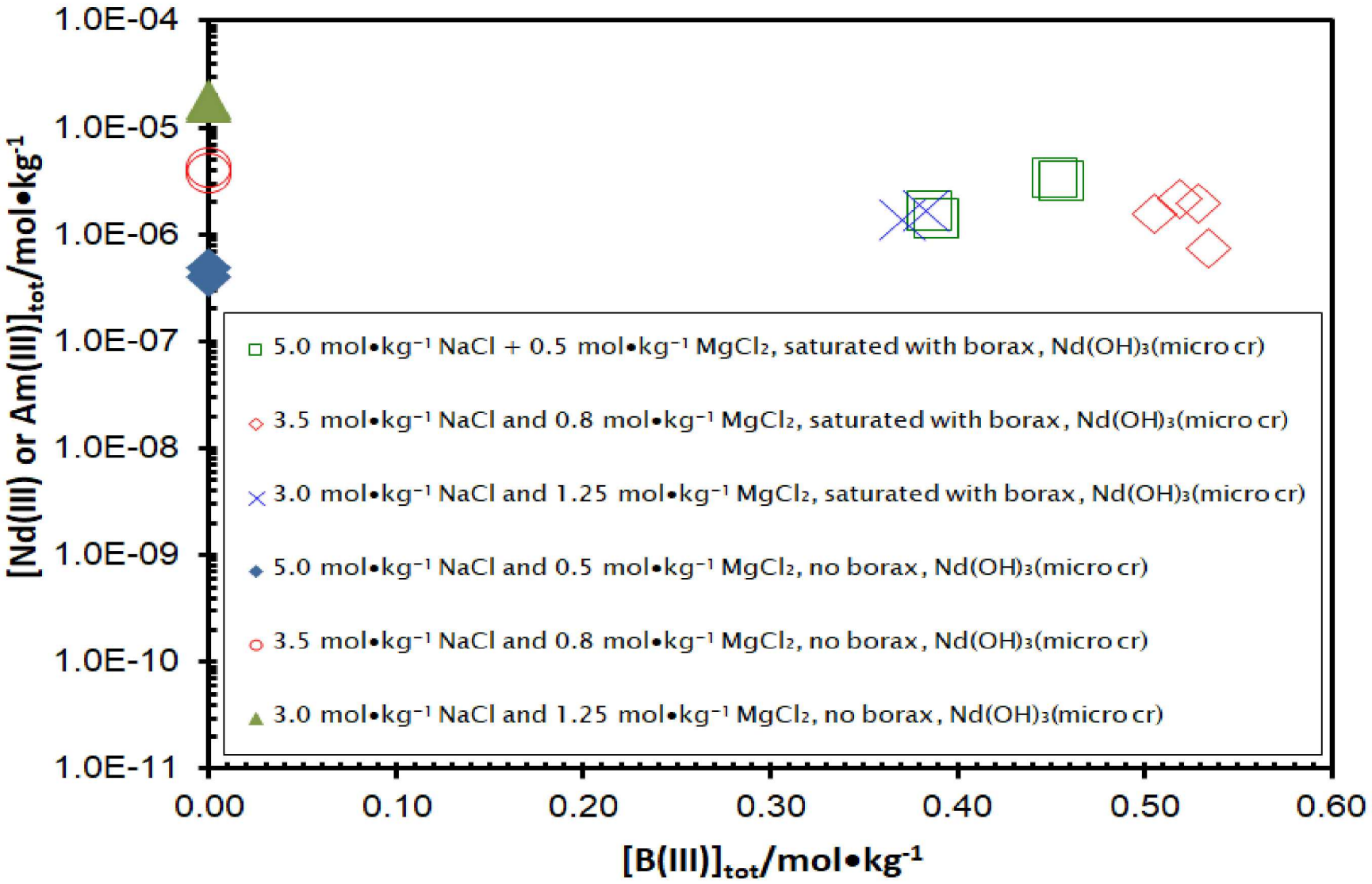
Solubility of Am(III)/Nd(III) in Mixtures of NaCl and $MgCl_2$ in the Presence of Borate



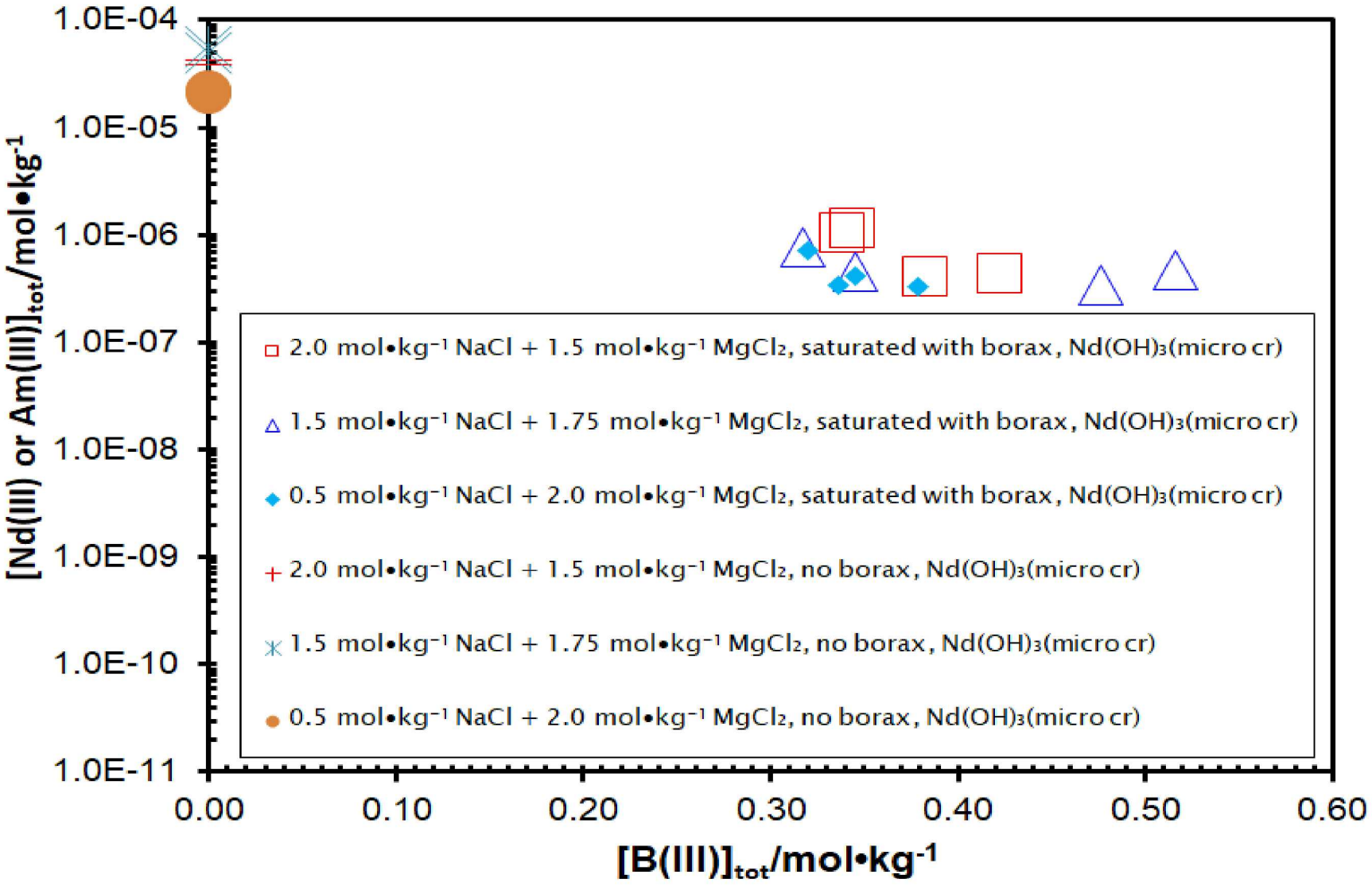
Solubility of Am(III)/Nd(III) in Mixtures of NaCl and $MgCl_2$ in the Presence of Borate



Solubility of Am(III)/Nd(III) in Mixtures of NaCl and $MgCl_2$ in the Presence of Borate



Solubility of Am(III)/Nd(III) in Mixtures of NaCl and $MgCl_2$ in the Presence of Borate



Summary

- In this work, we have conducted solubility measurements regarding $Nd(OH)_3$(micro cr) in mixtures of NaCl and $MgCl_2$ saturated with borax at 25°C.
- Our results indicate that in the NaCl-dominated brines, the presence of borate increases Nd(III) concentrations.
- Our results indicate that in the $MgCl_2$-dominated brines, the presence of borate decreases Nd(III) concentrations.